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(54) **Method for ortho-alkylation of hydroxyaromatic compounds.**(30) Priority: **03.06.83 US 500684**(43) Date of publication of application:
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tions Ltd., London, GB; & JP - A - 44 27 367
(MITSUI SEKIYU CHEM. IND.)

(73) Proprietor: **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady New York 12305(US)(72) Inventor: **Bennett, James Gordy, Jr.**
16 East Bayberry
Glenmont New York 12077(US)(74) Representative: **Catherine, Alain**
General Electric France Service de Propriété
Industrielle 18 Rue Horace Vernet
F-92136 Issy-Les-Moulineaux Cedex(FR)

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Description

This invention relates to a process for ortho-alkylation of hydroxyaromatic compounds with alkanols and resulting in decreased by-product formation during said alkylation.

Ortho-alkylated hydroxyaromatic compounds are known to be useful for various purposes. For example, 2-alkyl- and 2,6-dialkylphenols may be oxidatively coupled to yield polyphenylene oxides, some of which are used as constituents of engineering plastics.

A typical method for preparation of such compounds is by alkylation of the precursor hydroxyaromatic compound with a primary or secondary alkanol in the presence of a suitable catalyst. The use of magnesium oxide catalysts for this purpose is disclosed in U.S.- A -3,446,856 and 4,201,880. According to Japanese Kokai 69/27367, the selectivity of such catalysts for o-alkylation is improved by combining them with 0.5-50% by weight of copper or a similar metal.

Notwithstanding the above-identified disclosures, various problems still exist with the alkylation methods and the catalysts used therein. In the first place, the active life of many of these catalysts is undesirably short, sometimes less than 50 hours.

In the second place, many of such methods and catalysts still produce an undesirably high proportion of p-alkylated products of marginal utility. Thus, alkylation of phenol with methanol in the presence of magnesium oxide yields o-cresol and 2,6-xlenol, the desired products, but in addition yields substantial amounts of such p-substituted compounds as p-cresol, 2,4-xlenol and mesitol (2,4,6-trimethylphenol). These p-substituted compounds are much less useful than the corresponding compounds containing unsubstituted para positions, since they do not yield polymers with the desirable properties possessed by the polyphenylene oxides prepared from such compounds as 2,6-xlenol.

In the third place, the high temperatures (above 460°C and frequently above 500°C) required for alkylation using previously known catalysts require an undesirably high energy input and decrease catalyst life. In addition, such temperatures introduce other problems such as thermal decomposition of the reactants. For example, methanol is dehydrogenated under alkylation conditions to formaldehyde, a desirable reaction since the aldehyde is a necessary alkylation intermediate. However, at extremely high temperatures a substantial amount of formaldehyde decomposes to carbon monoxide and hydrogen. Such decomposition products are of little use except as fuel. It is strongly preferred to minimize decomposition of methanol and formaldehyde so as to enable their use for alkylation.

GB-A-1 153 890 describes the dehydrohalogenation of halohydrocarbon in the presence of a dehydrohalogenation-halide oxidation catalyst comprising an oxide of a metal selected from the group consisting of a magnesium, calcium, and zinc, composited with from 0.1 wt.% to 15 wt.% copper as a copper oxide.

US-A-3 466 856 describes a process for selectively methylating a phenol which comprises reacting methanol and phenol in the vapor phase in the presence of a magnesium oxide as the catalyst, said reaction being carried out at a catalyst bed temperature in the range of 475 - 600°C.

JP-A-4 427 367 describes the methylation of phenols with methanol in the presence of a catalyst comprising MgO and at least one of Cu, Zn, Ni, Mo, W, Be, Pt and Pd, the ratio of metal to MgO being 0.5 to 50 wt. %, using reaction temperature higher than 400°C, preferably 500-600°C. In example 1 it is reported that using a catalyst containing weight % Cu and a reaction temperature of 530°C there are obtained 95.5% phenol conversation ratio, a 67.1% 2,6-xlenol formation ratio and a 5.5% mesitol formation ratio.

Thus the object of the present invention is to provide an improved process for the ortho-alkylation of hydroxy aromatic compounds with alkanols using lower reaction temperatures and resulting in a high degree of selectivity for ortho-alkylation.

Other objects will in part be obvious and will in part appear hereinafter.

The above object is attained according to the present invention by providing a method for alkylating at least one hydroxy aromatic compound by the catalytic reaction of the same with at least one primary or secondary alkanol, characterized in that it comprises carrying out said reaction at a temperature up to 475°C in the presence of a catalyst composition which comprises magnesium oxide and up to 0.1 % by weight, based on said magnesium oxide, of copper, said copper being deposited on said magnesium oxide in elemental or chemically combined form in a layer of submicroscopic thickness.

The method for preparing a solid catalyst composition useful in the present invention comprises preparing, at a temperature within the range of 50 - 100°C, a slurry of (1) a substantially water-insoluble magnesium reagent which yields magnesium oxide upon calcination in (2) an aqueous solution of at least one copper salt, the copper content of said slurry being such that the copper content in the catalyst composition ranges up to 0.1% by weight, based on the magnesium oxide, thereby producing a

magnesium-containing solid phase with a copper-containing coating; removing and drying said solid phase; and calcining the same at a temperature within the range of 350-550 °C.

Any substantially water-insoluble magnesium reagent which yields magnesium oxide upon calcination may be used in the catalyst preparation method of this invention. The preferred reagents are magnesium oxide, magnesium hydroxide, magnesium carbonate and mixtures thereof. Magnesium oxide exists in an inactive "dead burned" and a "reactive" form; the latter is converted to magnesium hydroxide upon contact with water, and therefore it may be used according to this invention. Particularly useful as a magnesium reagent is basic magnesium carbonate, which is a commercially available material. It is also known as magnesium carbonate hydroxide and is identified in The Merck Index, Ninth Edition, in monograph #5483 as having the approximate formula $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

The copper salt may be either cuprous or cupric; cupric salts are generally preferred because of their ready availability. Illustrative copper salts are cuprous chloride, cupric acetate, cupric bromide, cupric chloride, cupric nitrate and cupric sulfate. Also included are coordination complexes of copper, exemplified by the complexes with ammonia and amines. The copper salt should have some solubility in water, but it need not be soluble in high proportions since a relatively small amount of it is used.

According to this invention, an aqueous slurry containing the copper salt and magnesium reagent is prepared, typically by gradual addition of an aqueous solution of the copper salt to a slurry of the magnesium reagent in water at a temperature of about 50-100 °C, preferably about 70-80 °C. The slurry thus obtained typically contains about 10-35% and preferably about 10-15% by weight of the magnesium reagent. The copper content thereof is such that the final catalyst composition has a copper content of up to 0.1% by weight and normally 0.02 to 0.04%.

The aqueous slurry prepared may be agitated, typically with heating within the same range, after addition of the copper salt. During this process the copper salt is deposited on the surface of the magnesium reagent in a layer of submicroscopic thickness. Preferably, the copper distribution on the magnesium reagent is relatively uniform; it has been found that the activity of the catalyst in the alkylation reaction decreases with a decrease in uniformity of the copper layer.

Following deposition of the copper on the magnesium reagent, the solid phase is separated, usually by filtration or centrifugation, and dried, usually by heating at a temperature up to about 200 °C, typically in a vacuum oven. For the sake of convenience of storage and use, it is frequently preferred to pelletize the solid phase after drying and before calcining. This is ordinarily effected by sieving (typically through a 25 mesh (0.71mm) sieve), milling and compressing. To facilitate pelletizing, binders, filler and/or pelletizing lubricants known in the art (hereinafter collectively designated "fillers") may be incorporated into the catalyst. Typical of these are graphite and polyphenylene oxide. The filler content of the pelletized solid may be up to about 25% by weight based on copper plus magnesium oxide, depending on the filler used; polyphenylene oxide is most often used in an amount up to about 20%, and graphite in an amount up to about 5%.

The solids are then calcined by heating at a temperature within the range of 350-550 °C. During calcination, the magnesium reagent is converted to magnesium oxide which is the active magnesium species in the catalyst. Calcination temperatures higher than about 550 °C are undesirable since they may result in sintering of the magnesium oxide, with a decrease in surface area and consequently in catalyst activity.

The active copper species in the alkylation catalyst is believed to be elemental copper. Therefore, it is important to reduce combined copper in the solids to the elemental state. Reduction may be effected before, during or after calcination, and the conditions of calcination determined accordingly. Thus the calcination atmosphere may be oxidizing (e.g., oxygen or air), inert (e.g., nitrogen) or reducing (e.g., hydrogen or other reducing agents). The presence of substances such as water, alkanol and hydroxyaromatic compound is also permissible.

Calcination in a reducing atmosphere is frequently preferred. For example, it may be effected in the presence of hydrogen, typically at 375-550 °C. It is often most preferred to calcine at 350-450 °C, preferably 360-380 °C, in contact with the alkanol-hydroxyaromatic compound feed stream for alkylation. The copper is then reduced by alkanol which is oxidized to the corresponding aldehyde, the essential alkylation intermediate.

In general, the solid catalyst compositions produced by the method of this invention comprise magnesium oxide and up to about 0.1% by weight, based on said magnesium oxide, of copper, said copper being deposited on said magnesium oxide in elemental or chemically combined form. It is believed that the copper layer is essentially monoatomic. Catalyst compositions of this type are also an aspect of the

*by weight, based on the magnesium oxide.

invention. The copper content therein, based on magnesium oxide, is up to 0.1% by weight and usually 0.02 - 0.04% by weight in terms of surface area, the preferred range of the catalyst composition is 50-400 and most often 100-250²/g. The surface area was measured by the BET method.

The preparation of the catalyst compositions useful in the present invention is illustrated by the following examples.

EXAMPLE 1

Basic magnesium carbonate, 400 grams, was added at 80°C, with stirring, to 2500 ml. of distilled water. The resulting slurry was stirred for 30 minutes at 80°C, after which a solution of 0.38 gram of cupric nitrate trihydrate in 200 ml. of water was added at the same temperature over one hour, with stirring. Heating and stirring were continued for two hours, after which time substantially no copper was left in the liquid phase. The mixture was filtered and the solids were dried in vacuum at 120°C for 16 hours.

The dry solids were broken up and put through a 25 mesh (0.71 mm) sieve. There was added 2 grams (0.5% by weight) of graphite and the mixture was milled in a jar mill, precompressed, reground to 25 mesh (0.71 mm) and pelletized in cylindrical pellets, 3/16 inch (4.76 mm) in diameter and 1/8 inch (3.75 mm) long. The tablets were calcined in an alkylation reactor during use by heating from 370°C to 440°C in the presence of a phenol-methanol feed (as described in Example 6) to yield the desired catalyst composition.

EXAMPLE 2

A catalyst was prepared by the procedure of Example 1 except that 8 grams (2% by weight) of polyphenylene oxide was added with the graphite prior to pelletizing.

EXAMPLE 3

A catalyst was prepared by the procedure of Example 1 except that 10% by weight polyphenylene oxide was incorporated therein and calcination and reduction were effected by heating at 500°C in a hydrogen atmosphere for 4 hours.

The hydroxyaromatic compounds which may be alkylated with the catalyst of this invention include all of such compounds which have a free ortho-position. Examples are phenol, 1-naphthol, 2-naphthol, o-cresol, m-cresol, p-cresol, 2,4-xyleneol, o-ethylphenol, p-isopropylphenol, p-n-butylphenol, 2,4-diethylphenol, catechol, resorcinol and hydroquinone. In general, any alkyl substituents will be primary or secondary, preferably primary, and will contain up to about 4 carbon atoms. The most preferred hydroxyaromatic compounds are the monohydroxyaromatic compounds and especially those in which the para-position is unsubstituted. Phenol, i.e., monohydroxybenzene, is the preferred hydroxyaromatic compound. o-Cresol, which is a by-product in the methylation of phenol to 2,5-xyleneol, is somewhat less preferred. Mixtures of any of these compounds may also be used.

The alkanol used for alkylation may be primary or secondary and is usually primary. It is most often a lower alkanol, that is, one containing up to 7 carbon atoms. Illustrative alkanols are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol and 1-hexanol. Especially preferred are alkanols containing up to 4 carbon atoms. For reasons of availability, cost and particular utility of the alkylated product, methanol is the most preferred alkanol.

Except when otherwise noted herein, the alkylation conditions used according to this invention are those described in the aforementioned U.S.- A -3,446,856 and 4,201,880. Pressures may vary from atmospheric to as high as about 150 psig (1.03×10^6 Pa), but usually need be no higher than about 30 psig (0.2×10^6 Pa). The proportion of catalyst with respect to reactants is conveniently defined in terms of liquid hourly space velocity (LHSV), which is the volume of liquid feed per unit volume of catalyst per hour, and is typically about 0.5-5.0 and preferably about 1.5-2.5.

The maximum alkylation temperature employed according to this invention is about 475°C. A typical alkylation temperature range is about 400-475°C and preferably about 420-450°C. For the most part, the temperatures within this range are substantially lower than those disclosed in the aforementioned patents. In addition to decreasing the necessary energy input, the use of these lower temperatures minimizes alkanol wastage.

The utility of the catalysts of this invention in the alkylation of hydroxyaromatic compounds is illustrated by the following examples. All percentages are by weight.

EXAMPLE 4

A reactor was loaded with 110 ml. of the catalysts of Examples 1 and heated to 370°C. The reactor was pressurized with nitrogen to 25 psig (0.17×10^5 Pa). and nitrogen was passed through as the temperature was increased to a maximum of 440°C. After 15 minutes, a mixture of 128 grams of methanol, 94 grams of phenol and 44 grams of water (4:1 molar ratio of methanol to phenol) was fed to the reactor at 215 ml./hr. (LHSV or 2.0). The alkylation was run for 502 hours, during which the yields of o-cresol, 2,5-xyleneol, p-cresol, 2,4-xyleneol and mesitol were monitored and weighted averages calculated. The selectivity of the catalyst, which is defined as the ratio of 2,6-xyleneol yield to combined yield of 2,4-xyleneol and mesitol, was determined from these average yields. Also measured was off-gas evolution in standard cubic feet per hour (SCFH), which is proportional to the amount of methanol decomposition to carbon monoxide and hydrogen. The results are given in Table I, compared with a control catalyst prepared by a similar procedure but containing 0.5% copper.

TABLE I

	Control	Ex. 1
2,6-Xyleneol, %	52.7	73.5
o-Cresol, %	23.0	13.4
p-Cresol, %	0.10	0
2,4-Xyleneol, %	1.12	0.38
Mesitol, %	9.7	8.4
Selectivity	4.74	8.23
Off-gas, SCFH (l/h)	0.68 (19.25)	0.40 (11.32)

As the data in Table I show, the selectivity of the catalysts of this invention is much higher than that of the control. Also, the catalysts of this invention given a substantially higher yield of 2,6-xyleneol than the control. Moreover, except in the case of Example 3 the off-gas production of the catalyst of this invention was substantially lower than that of the control.

EXAMPLE 5

Following the procedure of Example 4 except for an LHSV of 2.1, the catalyst of Example 2 was compared with a magnesium oxide catalyst similar to that disclosed in U.S.- A -3,446,856. The results are given in Table II.

TABLE II

	Control	Ex.2
2,6-Xyleneol, %	68.0	73.8
o-Cresol, %	17.7	14.6
p-Cresol, %	0.02	0.09
2,4-Xyleneol, %	0.20	0.20
Mesitol, %	6.0	6.4
Selectivity	10.96	11.18
Off-gas, SCFH (l/h)	0.40 (11.32)	0.44 (12.76)

The results in Table II show that while the selectivity and off-gas production of the copper-containing catalyst of this invention are comparable to those of the control, the yield of 2,6-xyleneol is substantially higher.

In addition to the above-described advantages, the catalysts of this invention are characterized by long active life, typically remaining active for 800 hours or more of use.

Claims

1. A method for alkylating at least one hydroxy aromatic compound by the catalytic reaction of the same with at least one primary or secondary alkanol, characterized in that it comprises carrying out said

reaction at a temperature up to 475 °C in the presence of a catalyst composition which comprises magnesium oxide and up to 0.1 % by weight, based on said magnesium oxide, of copper, said copper being deposited on said magnesium oxide in elemental or chemically combined form in a layer of submicroscopic thickness.

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2. A method as in claim 1, characterized in that the alkanol is methanol.
3. A method as in claim 2, characterized in that the hydroxy aromatic compound is a monohydroxy aromatic compound in which the paraposition is unsubstituted.
4. A method as in claim 3, characterized in that the hydroxy aromatic compound is phenol or o-cresol.
5. A method as in claim 4, characterized in that the alkylation temperature is 420 °C to 450 °C.

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15 Patentansprüche

1. Verfahren zur Alkylierung von wenigstens einer hydroxyaromatischen Verbindung durch katalytische Reaktion derselben mit wenigstens einem primären oder sekundären Alkanol, dadurch gekennzeichnet, daß es die Durchführung der Reaktion bei einer Temperatur bis zu 475 °C in Anwesenheit einer Katalysator-Zusammensetzung umfaßt, welche Magnesiumoxid und bis zu 0,1 Gew.-% Kupfer, bezogen auf das Magnesiumoxid enthält, wobei das Kupfer auf dem Magnesiumoxid in elementarer oder chemisch gebundener Form in einer Schicht von submikroskopischer Dicke abge-
schieden ist.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Alkanol Methanol ist.
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die hydroxyaromatische Verbindung eine monohydroxyaromatische Verbindung ist, in welcher die Parastellung unsubstituiert ist.
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die hydroxyaromatische Verbindung Phenol oder Orthocresol ist.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß die Alkylierungstemperatur 420 °C bis 450 °C beträgt.

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Revendications

1. Procédé pour l'alcoylation d'au moins un composé aromatique hydroxylé, par réaction catalytique dudit ou desdits composés avec au moins un alcanol primaire ou secondaire, caractérisé en ce qu'il comprend la réalisation de ladite réaction à une température atteignant au plus 475 °C, en présence d'une composition catalytique comprenant de l'oxyde de magnésium et jusqu'à 0,1 % en poids, par rapport audit oxyde de magnésium, de cuivre, ledit cuivre étant déposé sur ledit oxyde de magnésium sous forme élémentaire ou sous forme chimiquement combinée, en une couche d'épaisseur sous-microscopique.
2. Procédé selon la revendication 1, caractérisé en ce que l'alcanol est le méthanol.
3. Procédé selon la revendication 2, caractérisé en ce que le composé aromatique hydroxylé est un composé aromatique mono-hydroxylé qui n'est pas substitué en position para.
4. Procédé selon la revendication 3, caractérisé en ce que le composé aromatique hydroxylé est le phénol ou l'ortho-crésol.
5. Procédé selon la revendication 4, caractérisé en ce que la température d'alcoylation est de 420 °C à 450 °C.

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